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COMBUSTIVE APPROACH FOR MEASURING TOTAL VOLATILE PHOSPHORUS CONTENT IN LANDFILL GAS

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Abstract. A technique was developed to measure the total gaseous phosphorus content in biogas. The amount of air needed for a neutral to oxidising flame was mixed with the biogas. The gas mixture was burnt in a closed quartz burner and the combustion gasses were bubbled through a nitric acid solution. The phosphate content in the bubbling liquid was determined with sector field ICP-MS. The technique was validated in the lab with phosphine. Afterwards the set-up was installed on a landfill. The total gaseous phosphorus content in the landfill gas, measured with the combustive technique, ranged from 1.65 to 4.44 μg P/m^3. At the same time the phosphine concentration in the landfill gas was determined gas chromatographically (GC). The phosphine (PH_3) content measured with GC ranged from 7.6 to 16.7 μg PH_3-P/m^3. Since the phosphine-P content (GC) was consistently higher than the total gaseous phosphorus content (burner/ICP-MS), the hypothesised presence of highly toxic gaseous phosphorus compounds other than phosphine could not be demonstrated.

Keywords: phosphine, burner, total gaseous P, landfill

1. Introduction

Landfill gas is a product of the natural biological decomposition of organic material contained in wastes deposited in landfills. Keller (1988) postulated that all landfill gases contain the following six classes of compounds: saturated and unsaturated hydrocarbons, acidic hydrocarbons and organic alcohols, aromatic hydrocarbons, halogenated compounds, sulphur compounds such as carbon disulphide and mercaptans, and inorganic compounds. In addition, a number of methylated metal and non-metal compounds, inorganic volatile metals (e.g. Hg°) and hydrides of metals and metalloids have been detected in landfill gas (Feldmann *et al.*, 1998). Feldmann and Hirner (1995) investigated the presence of unstable volatile organometallics using GC-ICP-MS and detected volatile As (16–49 μg/m^3), Se (0.003–0.004 μg/m^3), Sn (8.62–35 μg/m^3), Sb (24–72 μg/m^3), Te (0.048–0.075 μg/m^3), Hg (0.049–0.130 μg/m^3), Pb (0.013–0.033 μg/m^3) and Bi (0.31–0.89 μg/m^3) compounds. Si and P could not be measured because of the high background at masses 28 (N_2^+, CO^+), 29 (N_2H, COH^+), 30 (NO^+) and 31 (NOH^+, $^{15}NO^+$).

Glindemann *et al*. (1996b) detected phosphine (PH_3) in gas from a landfill near Berlin, with a cryogenic trapping-GC-NPD system. The maximum concentration was 24.6 $\mu g/m^3$. The maximum observed concentration of phosphine in gas from a landfill near Beijing was 1.1 $\mu g/m^3$ (Ji-ang *et al*., 1999). With a similar system biogas from a series of anaerobic digestors and one landfill, situated in Flanders, was analysed. In comparison with the gas from digestors, the phosphine concentration in the landfill gas (6.4 $\mu g/m^3$) was by far the highest (Roels *et al*., 2002).

The origin of phosphine is still the subject of controversy (Roels and Verstraete, 2001). It is unclear whether phosphine is the only gaseous phosphorus compound present in fermentation gases (Dévai *et al*., 1988). At one occasion, diphosphine (P_2H_4) was reported to be released after alkaline digestion of liquid from an anaerobic batch experiment in which human faeces was the inoculum (Gassmann and Glindemann, 1993). Iverson and Olson (1983) postulated that the primary cause of anaerobic corrosion of iron was due to a volatile phosphorus compound. Both analytical attempts to identify the phosphorus gas and the fact that, according to the authors, phosphine was demonstrated to be non-corrosive to iron led to the conclusion that the compound of interest was not phosphine.

In this paper a combustive measurement technique for the determination of the total gaseous phosphorus content in landfill gas or biogas is presented. The landfill gas was mixed with the stoichiometric needed amount of air to obtain a complete combustion. The gas mixture was burned in a closed burner and the combustion gases were led through a bubbler filled with a nitric acid solution. Determination of the concentration of phosphate in the solution enabled the quantification of total gaseous phosphorus content in the landfill gas. The gaseous phosphorus concentration obtained with this new technique was compared with the gas chromatographically determined phosphine concentration in the landfill gas.

2. Approach

2.1. Burner design

A scheme of the burner and the set-up used on-site is drawn in Figure 1(6). The burner was made of quartz since borosilicate glass was not expected to resist the high temperatures generated by the flame. Stainless steel fittings, Teflon ferrules and tubing provided a completely inert flow-path. The inner-diameter of the burner head was 11.5 mm (outer diameter 14 mm).

2.2. Test 1: Technique validation at high concentrations

A certified gas standard cylinder containing 62.3 $\pm$ 1.87 mg/m^3 phosphine-P in nitrogen was purchased from Messer–Griesheim (Frankfurt, Germany). All other gases were also purchased from Messer. With the aid of a second pressurised

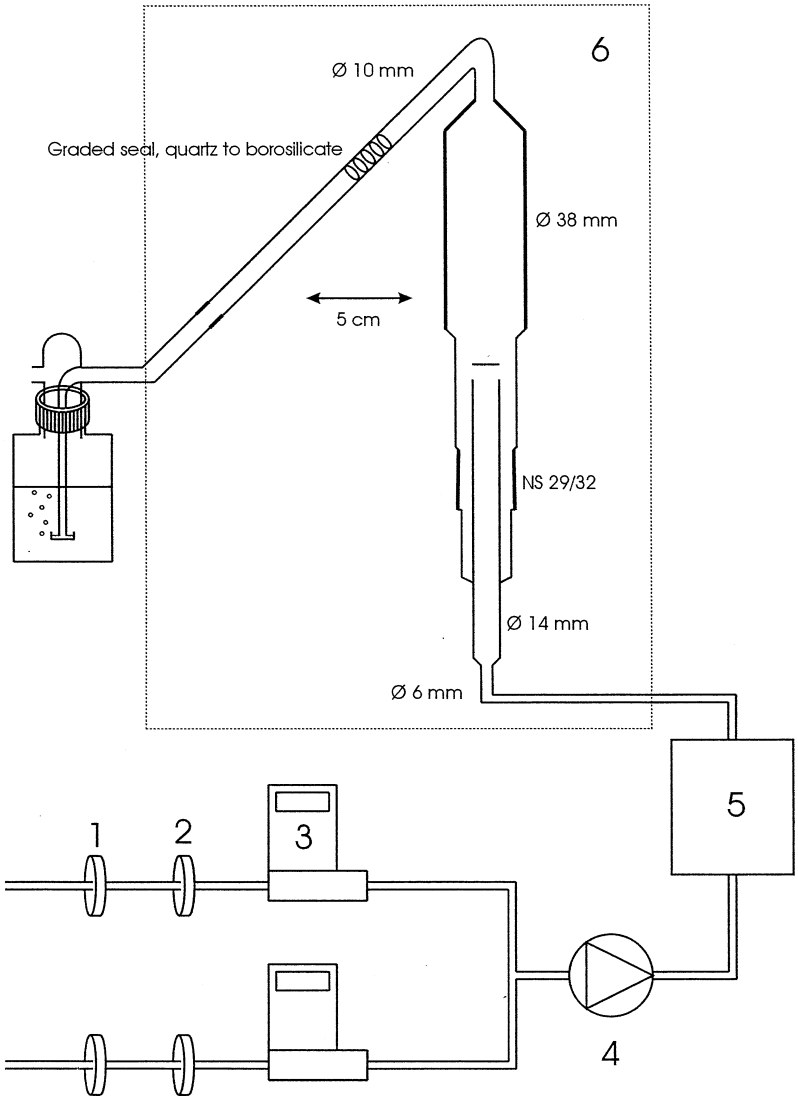

Figure 1. On-site set-up: (1) 1 μm glass filter (2) 0.2 μm Teflon filter (3) mass flow controller (4) membrane pump (5) buffer vessel to reduce pulsations. The scale is only valid within the dotted frame (6).

gas bottle containing 60% methane and 40% carbon dioxide and two mass flow controllers (MFC) (range: 0–100 mL/min and 0–5 L/min) (Sierra, Monterey, CA, U.S.A.), a synthetic biogas was composed containing 3.46 mg/m^3 phosphine-P, 56.67% CH_4, 37.78% CO_2 and 5.56% N_2. The flow rate of the synthetic biogas was set at 0.54 L/min. Ambient air, supplied by an air-pump (Rena, Annecy, France), was added to this synthetic gas. A third MFC (Bronkhorst, Ruurlo, The Netherlands)

was used to control the air flow rate at 2.89 L/min. The combustion gases passed through a bubbler (250 ml) containing 200 ml of a 1 M HNO_3 solution. High purity HNO_3 (trace select, phosphate conc. $\leq$0.01 mg/kg) (Fluka, Bornem, Belgium) and milli-Q water (Millipore, Brussels, Belgium) were used to prepare the solution. The bubbler was placed in a warm water bath set at 64°C. Typically, an experiment lasted approximately 50 min. After each experiment the inner surface of the quartz/glass burner was rinsed several times with the bubbling liquid. After rinsing the volume of the bubbling solution was determined. Based on the set phosphine-P concentration in the synthetic gas, the synthetic gas flow rate (0.54 L/min) and the bubbling liquid volume, the expected phosphate-P concentration was calculated. The increase or decrease in volume was taken into account during the calculations. The phosphate concentration in the bubbling liquid was measured spectrophotometrically using a commercially available test kit (Merck, Leuven, Belgium) (range: 0.01–5 mg/L PO_4^{3-}-P). Before adding the reagents, the pH needed to be adjusted to neutrality with KOH (10 M).

Between experiments, a rigorous cleaning procedure was followed. The set-up was soaked overnight in a 1 M HNO_3 solution and cleaned afterwards times with milli-Q water.

2.3. Test 2: Technique validation at low concentrations

A second series of experiments was performed in which the synthetic biogas composition was set at: 59.07% CH_4, 39.38% CO_2, 1.56% N_2 and 0.97 mg/m^3 phosphine-P. The set-up and the rinsing of the set-up with the bubbling liquid was the same as discussed in the previous section. The cleaning procedure was different in that the set-up was not soaked overnight in an 1 M HNO_3 solution but, instead rinsed three times with milli-Q water immediately after each experiment. An experiment lasted approximately 8 min. The phosphate-P concentration was measured with sector field ICP-MS. The same analytical procedure, but this time using a synthetic biogas without phosphine, was followed for the blank determinations.

2.4. Test 3: On-site measurements

Subsequently, the set-up was moved to the landfill Hooge Maey. The Hooge Maey landfill is the largest municipal solid waste landfill (surface: 35 hectares, height up to 41 m) in Flanders. It is situated north of the city of Antwerp. At the time of testing a section of the landfill was equipped with an active gas collection system. A pilot-scale burner was operated to evaluate the feasibility of energy recovery at the Hooge Maey landfill. A minute side-stream of the collected gas was drawn off at a section before the condenser which was positioned in front of the compressor. A scheme of the set-up used on-site is drawn in Figure 1. The landfill gas and ambient air were suctioned with a membrane pump through a 1 μm glass pre-filter (Type A/E, Pall, Ann Arbor, U.S.A.) and a 0.2 μm PTFE filter (TF, Pall). Flow rates were

controlled with MFC's. An extra buffer vessel (volume 3 L) was installed to reduce the pulsations of the pump. A platinum wire (diameter: 1 mm, length: 5 cm) (Alfa Aesar, Karlsruhe, Germany) was attached onto the burner head to reduce the risk of the flame being blown out.

A typical experiment lasted approximately 24 hours. Rinsing and cleaning was the same as in Test 2. The phosphate-P concentration was measured with sector field ICP-MS. After each experiment the filters were replaced. Before and after each experiment the phosphine concentration in the landfill gas was measured with GC-TSD (Thermionic Specific Detector).

2.5. Sampling and gas chromatographic conditions

Plastic syringes (60 ml) (BD, Erembodegem, Belgium) , Tedlar gas sampling bags (5 L) (Alltech, Lokeren, Belgium) and evacuated (−100 kPa) pressure resistant Duran glass bottles (Schott Glas, Mainz, Germany) with a volume of 1 L, equipped with open top screw cap (GL 45) and butyl rubber sealing (Rubber BV, Hilversum, The Netherlands) were used for the sampling of gases. Landfill gas composition and phosphine concentration was determined using a gas chromatograph equipped with two detectors (TCD and TSD). The system has been described previously (Roels *et al.*, 2002). Cryogenic trapping of the gas samples was not necessary since the phosphine concentration in the landfill gas exceeded the limit of detection when a 500 μl sample loop was used.

2.6. Sector field ICP-MS

All measurements were carried out using a Finnigan MAT Element double-focusing sector field ICP-mass spectrometer (Giessmann and Greb, 1994). The Finnigan MAT Element is equipped with a sector field mass spectrometer of reversed Nier–Johnson geometry and hence, offers the capability to measure at higher mass resolution settings (Jakubowski *et al.*, 1998). As a result, this instrument is often called a 'high resolution' ICP-mass spectrometer. For all measurements carried out in the context of this work, the medium mass resolution setting ($R = 3000$) was used to separate the $^{31}P^{+}$ analyte signal from those of $^{14}N^{16}OH^{+}$ and $^{15}N^{16}O^{+}$ and hence, enable interference-free P determination. Sample introduction was accomplished by means of a Meinhard Tr-30-A3 concentric nebuliser mounted onto a water-jacketed double-pass Scott-type spray chamber, maintained at 4°C by means of a recirculating refrigeration/heating system and drained by the peristaltic pump. Sample solution was pumped to the nebuliser at a constant rate of approximately 1 mL/min. Nebuliser gas flow rate and electrostatic lens settings were optimised aiming at maximum signal intensity and optimum peak shape. The rf power was set at 1200 W. Both sampling cone and skimmer were manufactured from Ni.

The element used in this study was upgraded with a CD-1 interface, consisting of a grounded Pt ring mounted in-between the load coil and the ICP torch

(Appelblad *et al.*, 2000). Owing to the possibility to capacitively decouple the latter two components, the ion transmission efficiency, and hence, the signal intensity is improved by an order of magnitude as a result of a narrower energy distribution of the ions extracted from the ICP. Connecting/disconnecting this Pt ring from ground can be easily accomplished via the instrument's operation software.

In addition to the $^{31}P^{+}$ signal, that for $^{45}Sc^{+}$ was monitored. An equal concentration of Sc (10 μg/L) was present in all blank, sample and standard solutions and the signal intensity for $^{45}Sc^{+}$ was used as an internal reference, permitting correction for matrix effects (matrix-induced signal suppression or enhancement (Vanhaecke *et al.*, 1996)), signal drift and instrument instability. A measurement consisted of 40 consecutive 'passes', each lasting approximately 1 s, such that a measurement was completed in $<$1 min. For each sample, three replicate measurements were carried out. External calibration was accomplished using a 50 μg/L P standard.

3. Results

3.1. Test 1: Technique validation at high concentrations

The maximum total flow rate (=synthetic gas + air) is dependent upon the inner diameter of the burner and the composition of the gas. Preliminary results showed that a flame speed of 0.55 m/s (assuming a flat flame), resulting in a total gas flow of 3.43 L/min gave a stable flame at a mixing ratio air/methane of 9.53 which is the stoichiometric mixing ratio for a perfect combustion:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

Burning 0.54 L/min of synthetic biogas results in the formation of 27 g/h of H_2O. The saturated vapour pressure of pure water at 55°C exceeds the expected water vapour pressure in the combustion gases. In reality, the bubbling liquid needed to be heated to a temperature of 64°C to prevent condensation of water vapour and subsequently, overflow. The results obtained during this first test are presented in Table I. The average recovery obtained during these first tests was 66 $\pm$ 13%. Additionally, an experiment was carried out in which the phosphate-P concentration in the bubbling liquid was measured without rinsing the inner surface of the quartz/glass burner several times with the bubbling liquid. The recovery was only 5%. This proved that rinsing was very important. During the experiments gas samples of the combustion gases leaving the bubbler were analysed with GC-TSD. The phosphine concentration was below detection limit ($<$1 μg/m^3) in all cases.

3.2. Test 2: Technique validation at low concentrations

The results of the second test are presented in Table II. All sector field ICP-MS analyses were performed in duplicate. The observed PO_4^{3-}-P concentration

TABLE I
Results of the technique validation tests at high concentrations

Experiment no.	Expected (mg P/L)	Measured (mg P/L)	Recovery (%)
1	0.478	0.342 ± 0.001	71.5
2	0.484	0.359 ± 0.004	74.5
3	0.500	0.276 ± 0.002	55.3
4	0.513	0.324 ± 0.009	63.2

TABLE II
Results of the technique validation experiments at low concentrations (maximum RSD: 7%)

	Expected (μg P/L)	Measured (μg P/L)	Corrected (μg P/L)	Recovery (%)
Bubbling liquid[a]	0.23	2.33		
Blank 1[b]	0.23	3.22		
Blank 2	0.23	2.65		
Blank 3	0.23	3.03		
Experiment 1	12.67	9.66	6.69	53
Experiment 2	12.78	11.01	8.04	63
Experiment 3	12.15	11.93	8.96	74
Experiment 4	12.58	11.93	8.96	71
Experiment 5	12.18	11.81	8.84	73
Experiment 6	12.24	13.53	10.56	86

[a] Freshly prepared 1 M HNO_3 solution.
[b] Blanks are burner experiments without addition of phosphine to the synthetic biogas.

in the freshly prepared high purity 1 M HNO_3 solution was 2.33 μg P/L, while a concentration of 0.23 μg P/L was expected. The fact that a higher than expected signal was observed can be due to memory effects, instrumental background and possibly, contamination during the preparation of the solution. Three burner experiments in which no phosphine was added to the synthetic biogas (blanks) were carried out. The measured average phosphate-P concentration, in the bubbling liquid was 2.97 ± 0.37 μg/L. This average value was subtracted from the concentrations obtained after the regular experiments (measured concentration, Table II). This led to the corrected concentrations (Table II). Corrected concentration/Expected concentration $\times$ 100 = Recovery (%). A gradual increase in recovery was observed in the course of experiments. On average the recovery was $70 \pm 11\%$.

Based on the data of the blanks a theoretical detection limit was calculated. Detection limit = 3 $\times$ standard deviation = 1.11 μg P/L.

TABLE III
Testing of different sampling devices for phosphine-inertness

	Day 1	Day 2
Plastic syringes	12.81 ± 0.57	11.3 ± 0.51
Butyl rubber stoppered glass bottles	13.69 ± 0.57	11.47 ± 0.01
Tedlar gas sampling bags	14.27 ± 0.08	12.05 ± 0.35

3.3. TEST 3: SAMPLING/ON-SITE MEASUREMENTS

Prior to the start of the on-site burning experiments, a short preliminary test was performed with the aim of finding a suitable sampling device. Landfill gas was sampled with plastic syringes ($n = 3$), evacuated glass bottles ($n = 3$) with butyl rubber septa and Tedlar gas sampling bags ($n = 3$) on two different days. The time between sampling and gas chromatographic phosphine determination was approximately 4 hours. In Table III the results of this test are shown.

On both days the same pattern was observed: the highest concentration of phosphine was measured after storage in Tedlar bags. The phosphine concentration in landfill gas stored in plastic syringes was the lowest. The difference between the three sampling devices was quite small and although all three were suitable, Tedlar gas sampling bags were used from then onwards. Much larger differences, between the three sampling devices, were observed when H_2S was to be determined (GC method described in Roels *et al*. (2002)). The H_2S concentration in the landfill gas stored in the glass bottles was 28% lower in comparison with storage in Tedlar bags. Plastic syringes contained 84% less H_2S than Tedlar bags after 4 hours of storage (data not shown).

The results of the on-site tests are presented in Table IV. The composition of the gas fed to the burner fluctuated quite strongly. Water from condensation accumulated in certain sections of the gas pipes responsible for the collection of the landfill gas causing a larger than normal underpressure in the gas collection system. This underpressure allowed a substantial amount of ambient air to enter the gas collection system through leaks in the pipes. Because of the blockage of pipes by condensation water, from time to time, the gas entering the burner came from different extraction wells. This was reflected by the quite large fluctuations in phosphine concentration.

Because the total gaseous phosphorus content of the landfill gas, measured with the burner, was lower than the phosphine-P content, measured with GC, an alternative approach was used enabling the interpretation of the acquired data. Starting from the assumption that phosphine was the only gaseous P compound, an expected concentration could be calculated with the following formula: Expected concentration = Phosphine concentration ($\mu g/m^3$) $\times$ Duration experiment (h)

TABLE IV

Results of the measurements at the Hooge Maey landfill. Recoveries are calculated starting from the assumption that phosphine was the only gaseous phosphorus compound present in the gas

	Landfill gas composition					PH_3-P conc.[d]		Expected conc.[e] (Min/Max)	Measured conc.[f]	Calculated gaseous P conc.[g]	Recovery[h] (Min/Max)
	Time[a] (h)	CH_4 (%)	CO_2 (%)	Air[b] (%)	Duration test[c] (h)	Time[a] (h)	PH_3-P (μg/m^3)	(μg P/L)	(μg P/L)	(μg P/m^3)	(%)
Exp. 1	0	59	40	1	24	24	13.0	47.7/47.7	6.1	1.65	13/13
	21	47.7	32.8	19.5							
	24	55.7	37.6	6.7							
Exp. 2.	−2	51.8	34.1	14.1	19	0	11.0	23.0/30.3	4.8	1.74	16/21
	16	52.7	35.2	12.1		22	8.3				
	20	53.5	37.7	8.8							
Exp. 3	0	53.5	37.7	8.8	26	0	8.3	34.1/65.5	10.3	2.50	16/30
	19	52.2	38.2	9.6		26	16.0				
	26	58.4	42.2	0							
Exp. 4	0	58.4	40.9	0.7	23	0	16.7	26.1/58.9	12.3	3.31	21/47
	23.5	57.9	41.5	0.6		23.5	7.4				
Exp. 5	0	59.3	41.2	0	23.5	−1	10.6	39.6/42.6	15.6	4.44	37/39
	16	45	32.4	22.6		24	11.4				
	23	60.8	42.2	0							

[a] Negative values stand for measurements prior to a burner experiment.
[b] Air = Nitrogen + Oxygen.
[c] Duration test = duration of a burner experiment.
[d] Measured with GC.
[e] Calculated as duration of burner experiment × landfill gas flow rate × PH_3-P conc. measured with GC/bubbling liquid volume.
[f] PO_4^{3-}-P conc. in bubbling liquid/corrected for blanks (Table II).
[g] (Bubbling liquid PO_4^{3-}-P conc × bubbling liquid volume)/(duration × landfill gas flow rate).
[h] Total gaseous P conc. (burner)/gaseous PH_3-P conc. (measured with GC).

$\times$ Landfill gas flow rate (m^3/h)/Volume bubbling liquid (L). Before and after each test the phosphine concentration was measured with a GC resulting in two expected concentrations (in Table IV, the lower of the two expected concentrations was classified as Min and the higher as Max). In all cases the measured concentration was lower than the expected concentration. Recovery (100 $\times$ measured/expected conc.) never exceeded 47%. Again, a gradual increase in recovery was observed in course of the experiments.

4. Discussion

It was already mentioned in the introduction that the gas from a number of digestors, analysed previously with the cryotrapping-GC-TSD system (Roels *et al.*, 2002), contained much less phosphine than landfill gas. The landfill site was chosen to test the combustive method since it was expected that a quantifiable amount of phosphate would accumulate in the bubbling liquid after operating the burner for a period of 24 hours even if phosphine was the only phosphorus compound present in the gas. It was addressed previously that it is still unclear whether, apart from phosphine, other phosphorus containing gases are present in fermentation gas.

Adding the platinum wire to the burner was necessary to keep the flame lit for a long time. The results obtained during the first and second lab-test showed that the measurement technique was quite accurate and reproducible in lab conditions. The technique could only be validated with phosphine because other possibly present phosphorus gases in landfill gas such as diphosphine, methylphosphine, and dimethylphosphine, are at present not commercially available. Recovery increased gradually during the second lab-test, indicating a possible memory effect. This presumed memory effect was not observed in the first test probably because of the more rigorous cleaning procedure in-between measurements.

The alleged presence of gaseous P compounds other than phosphine in fermentation gases could not be demonstrated with the on-site measurements. Calculated total gaseous P concentrations never exceeded the phosphine-P concentrations measured with the GC system. Similar to the second test, an increase in recovery (calculated, based on the assumption that phosphine was the only P compound present) was observed with every experiment, again, indicative for a memory effect. It is assumed that the lower recoveries obtained on-site were caused by the much lower phosphine concentrations in the landfill gas compared with the synthetic biogas used during test 2 (factor 100) and by the much more complex matrix. After 24 hours of operation a reddish, turning to yellowish, precipitate had formed in the upper part of the transfer line of the burner. The precipitate did not disappear after rinsing with the bubbling liquid and with strong acids (37% HCl, 65% HNO_3, 95% H_2SO_4). This precipitate might have been responsible for the lower recoveries compared to test 2. Elemental phosphorus (red, white, black), most phosphorus

sulphides (P_4S_7, P_4S_{10}) and phosphorus oxysulphides ($P_4O_6S_4$, $P_2O_2S_3$) react with strong acids. Possibly the precipitate contained P_4S_3 (used in the manufacturing of matches). It is known that, in the cold, P_4S_3 does not react with HCl or H_2SO_4. HNO_3, however, is believed to cause formation of elementary sulphur and various oxyacids of phosphorus (Van Wazer, 1964).

In the past, a number of oxidative methods were developed aimed at the measurement of phosphine. Tsubota (1959) used a 5 N nitric acid solution to oxidize phosphine to phosphate. Preliminary tests showed that this solution oxidised phosphine too slowly to be suitable for our goal (data not shown). Bruce *et al*. (1962) oxidised phosphine to phosphate with a Br_2 solution. Since bromine reacts with methane, it can not be used for the determination of phosphine in a landfill gas matrix. $HgCl_2$ solutions or mercury chloride coated on silica gel were also used to measure phosphine in air (Berck, 1968; Matsumura *et al*., 1990). Mercury chloride is not applicable for the determination of phosphine in landfill gas since H_2S reacts with Hg^{2+}. Filters impregnated with silver nitrate also suffer from H_2S interference (Demange *et al*., 2000). H_2S can be removed from the landfill gas by bubbling through a caustic solution (concentrated KOH). Bubbling, to avoid interference, followed by a known method was not the right option though, because it was not known whether the unknown gaseous phosphorus compounds we also wanted to measure, react with a caustic solution. It is also unclear whether the presumably present unknown gaseous phosphorus compounds in the landfill gas react with Ag^+ or Hg^{2+}. From the latter it is clear that the known 'wet chemical' methods, developed to measure phosphine in air, are not suitable to measure the total gaseous P content in fermentation gas.

No attempts were made to detect gaseous phosphorus compounds other than phosphine, in biogas, by means of gas chromatography. It is known that the gaseous and volatile organic phosphines are all very reactive substances (Van Wazer, 1964) and oxidation or reaction of the latter compounds during transfer of the gas from the sampling site to the lab was expected. Dietmar Glindemann tried to bypass the instability of organophosphines by using a transportable GC, but neither methylphosphine, dimethylphosphine nor trimethylphosphine was detected in landfill gas (personal communication). Instability of the compounds and personal communication with Dietmar Glindemann did not justify attempts to measure the unknown P compounds with GC.

Dévai *et al*. (1988) developed a technique similar to the one described in this paper. The gas mixture released from an Imhoff tank was burnt and the flue gases were quantitatively absorbed in reagent grade sodium hydroxide. They reported a volatile P concentration in the biogas of 31.5 mg P/m^3. It is striking that this value is a factor 1000 higher compared to the concentrations reported in numerous articles published since then. For a review on the subject the reader is referred to Roels and Verstraete (2001). The phosphate content was measured with the usual colorimetric method susceptible to arsenate interference (Murphy and Riley, 1962). However arsenate interference alone can not explain the extremely high values reported by

Dévai *et al*. (1988) since arsenic compounds are usually present in fermentation gas at $\mu g/m^3$ levels (Cullen and Reimer, 1989; Feldmann and Hirner, 1995).

Glindemann *et al*. (1996a) looked at the elemental content of oxide deposits in landfill gas and biogas fired power stations. Based on the assumption that 1 million m^3 produces 10 kg of deposit, Glindemann *et al*. calculated that the volatile P concentration in the landfill gas ranged from 2.4 to 22 $\mu g/m^3$. Those values were compared with gas chromatographically determined phosphine concentrations. The authors noted however that the validity of the correlation was limited, as samples from different landfills and times were compared.

5. Conclusion

Dévai *et al*. (1988) reported on extremely high phosphine concentrations in fermentation gas. It is striking that this value is a factor 1000 higher compared to the concentrations reported in numerous articles published since then. In a number of publications it was hypothesised that apart from phosphine, other P containing compounds could be present in fermentation gas. Possibly the gaseous P compound measured by Dévai *et al*. (1988) was not phosphine.

Gaseous organic phosphines are rather toxic as a class. The derivatives with the lowest boiling point, most closely related to phosphine itself —derivatives such as monomethylphosphine — are extremely toxic (Van Wazer, 1964). The known 'wet chemical' methods and GC are not suitable to measure gaseous P compounds, other than phosphine, in fermentation gas. A new combustive, interference free method, with relatively low recoveries, was developed to measure total gaseous P in landfill gas. Since the total gaseous P content in the landfill gas, measured with the burner, was lower than the phosphine-P content, the presence of unidentified gaseous P compounds could not be demonstrated. Possible explanations:

1. Phosphine is the only gaseous P compound in the landfill gas.
2. Other gaseous P compounds are present but the recovery of the combustive method is too low to prove their existence.

The data gathered during this work do not support the thesis that gaseous P compounds other then phosphine are responsible for the high concentrations reported by Dévai *et al*. (1988).

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